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Lisbeth M. Ottosen[a]; Pernille E. Jensen[a]; Henrik K. Hansen[b]; Alexandra Ribeiro[c]; Bert Allard[d]
[a] Department of Civil Engineering, Technical University of Denmark, Lyngby, Denmark [b] Departamento de Procesos Químicos, Biotecnológicos y Ambientales, Universidad Técnica Federico Santa María, Valparaíso, Chile [c] Departamento de Ciências e Engenharia do Ambiente, Faculdade de Cadencies e Technologia, Universidade Nova de Lisboa, Caparica, Portugal [d] MTM Forskningscentrum, Örebro Universitet, Örebro, Sweden

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Electrodialytic Remediation of Soil Slurry–Removal of Cu, Cr, and As

Lisbeth M. Ottosen,[1] Pernille E. Jensen,[1] Henrik K. Hansen,[2] Alexandra Ribeiro,[3] and Bert Allard[4]
[1]Department of Civil Engineering, Technical University of Denmark, Lyngby, Denmark
[2]Departamento de Procesos Químicos, Biotecnológicos y Ambientales, Universidad Técnica Federico Santa María, Valparaíso, Chile
[3]Departamento de Ciências e Engenharia do Ambiente, Faculdade de Cadencies e Technologia, Universidade Nova de Lisboa, Caparica, Portugal
[4]MTM Forskningscentrum, Örebro Universitet, Örebro, Sweden

Abstract: Severe soil contamination is often found at old wood preservation sites and a common combination of pollutants is Cu, Cr, and As. In the present work it is tested if simultaneous removal of Cu, Cr, and As can be obtained in an electrodialytic cell where the polluted soil is remediated as a stirred suspension (placed as the desalination compartment in accordance to the position of the ion exchange membranes). The soil for the experiments was sampled at an abandoned wood preservation site and contained 2170 mg Cu/kg, 710 mg Cr/kg and 3200 mg As/kg. SEM-EDX analysis showed that Cu, Cr, As and oxygen formed particles that were cementing soil minerals together. The soil was suspended in distilled water, distilled water with I_2 crystals to have an oxidizing environment, or in an acidified environment at pH about 1.0. The experiments lasted from 1 to 3 weeks. Good results were obtained in two experiments; an experiment where the soil was suspended in distilled water and the remediation lasted 3 weeks with 2.5 mA and an experiment with acidification of the soil suspension with HNO_3 to pH about 1.0 (2 weeks and 5 mA). The best separation of pollutants and soil was obtained in the experiment with suspension in distilled water. Based on soil concentrations, good Cu removal

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Address correspondence to Lisbeth M. Ottosen, Department of Civil Engineering, Techncial University of Denmark, Building 118, Lyngby 2800, Denmark. Tel.: +45 45252260. E-mail: lo@byg.dtu.dk

(95%) was obtained in both experiments. Removal of Cr was most efficient from the acidified soil suspension (74%). Both Cu and Cr concentrations were below the limiting values after the remediation. The As concentration, however, was not even although 61% was removed. In the soil remained about 1070 mg As/kg soil and since the limiting value is 40 mg As/kg, the removal was not efficient enough. So simultaneous removal was possible, but the target values were only met in the case of Cu and Cr, and more research is needed to remove As to a sufficiently low concentration, as well.

Keywords: Electrokinetics, electromigration, heavy metals, soil pollution, wood preservation

INTRODUCTION

For decades the most commonly used inorganic wood preservative worldwide was CCA (chromated copper arsenate). Spill of CCA at the production sites has resulted in severe soil pollution, especially at the old sites (1), (2). Unfortunately, there is no remediation method available to remove such combination of pollutants from soil and the aim of the present paper is to investigate the possibility for using an electrodialytic method where the soil is treated as suspension and also to optimize the method to exactly the pollution combination of Cu, Cr, and As.

Previously, electrodialytic removal of Cu from soil polluted from wood preservation industry in unenhanced laboratory scale has shown successful (unenhanced here means no addition of enhancement solutions to the soil but utilization of the acidic front developing from the anode to aid the heavy metal desorption). The best removal percentages reached are 98% from a Danish wood preservation soil (3) and 82% from a Portuguese soil (4), both obtained with an electrodialytic setup.

On the other hand, the success with electrokinetic and electrodialytic removal of As from soil polluted from wood preservation in un-enhanced systems has been limited, e.g. removal of 35% As was obtained in only 1.5 cm in an experiment that lasted for 42 days (5) and 51% As was removed from a Portuguese soil during 35 days (6). Desorption of As is highly dependent on both redox potential and pH. The primary forms of As in soils are arsenate As(V) and arsenite As(III), and under moderately reducing conditions, As(III) is the predominant form whereas at higher redox levels the predominant form is As(V). The experiments made so far were conducted in closed laboratory cells and As(III) is expected to be the primary form and the main stable species in an reducing environment at neutral to acidic pH is the uncharged (H_3AsO_3) (7) and since it is uncharged it is not mobile with electromigration, which may be the major problem in relation to the inefficient As removal.

In soils Cr is present in two different valences; Cr(III) and Cr(VI), dependent on the soil environment. In general Cr(III) is less mobile in soils than Cr(IV) and in soils Cr(III) is often predominant since Cr(VI) is a strong oxidizing agent and is often reduced to Cr(III) by the soil organic matter. Experiments with electrodialytic remediation of wood preservation soils have shown that Cr is strongly bound to the soil and difficult to remove, e.g. 13% Cr removed from a Portuguese soil during 38 days of remediation (6) and an even lower removal percentage of about 10% was reached during a 70 days experiment with a Danish wood preservation soil (8).

In unenhanced electrokinetic systems in-sufficient removal of Cr and As from soil polluted from wood preservation has thus been the result. The mixed pollution with Cu, Cr, and As is not straightforward to remediate with an electrochemical method since the behavior of the three pollution components is very different. To have a successful and simultaneous removal of the pollutants they must be desorbed during the remediation process and be present in ionic form in the soil solution. Cu and Cr(III) are in ionic form in an acidic environment but here As(III) is mainly present in uncharged species. Under alkaline conditions, however, charged As(III) species are prevailing (7) and thus As(III) is mobile in the applied electric field at high pH. Under aerobic conditions for pH higher than 2, As(V) will be an anionic species and thus mobile for electromigration at a wide pH range. In (8) it was shown that the addition of NaOH to a sandy loam polluted with As from wood preservation increased As mobility in the applied electric field significantly compared to an experiment with no pretreatment of the soil. This is in agreement with the work from (9) who found that alkaline conditions favored As electromigration in a spiked soil. Under alkaline conditions neither Cr(III) nor Cu is in ionic form, though Cr(VI) is, e.g. in spiked clays Cr(VI) was removed more efficiently from a glacial till than from kaolinite due to the higher pH in the glacial till throughout the remediation (10). Summing up, under reducing conditions there is no optimum pH where all three pollution components are mobile in the electric field at the same time, but under aerobic conditions there is a possibility at relatively low pH.

Addition of enhancement solutions to the wood preservation soils in connection with electrochemical remediation has been tested. Ammonia showed promising results in the case of Cu and As removal from a loamy sand polluted from wood preservation (5). Cu formed the charged tetramine complexes, As was mainly mobile due to the alkaline environment, and Cu and As were removed at the same time. For soils polluted with As and Cr sodium hypochlorite and the hydroxide ions produced at the cathode was used as desorbing agent (9). The hypochlorite oxidized the Cr(III) to the more mobile Cr(IV), which forms anionic species in the alkaline medium. Both As and Cr was removed as anions in this case. For soils polluted with all three elements Cu, Cr, and As neither ammonia nor sodium hypochlorite can be used. In this case ammonium citrate has shown potential and experimentally 33% Cr, 65% Cu, and 66% As was removed from a highly contaminated soil (11). In the present work it was investigated whether simultaneous removal of Cu, Cr, and As from a polluted wood preservation soil could be obtained during electrodialytic treatment. The effects of changes in the environment of the suspension (oxidizing and acidic conditions) on the removal efficiency were tested.

ELECTRODIALYTIC REMEDIATION OF SOIL IN SUSPENSION

In the present paper a modified electrokinetic soil remediation method was tested for remediation of a soil sampled at a wood preservation site. The soil was treated in suspension in an electrodialytic cell. The electrodialytic remediation method differs from electrokinetic remediation in the use of ion exchange membranes for separation of soil and solution in the electrode compartments. By the use of ion exchange membranes the main direction for the electromigration within the polluted soil is determined to be out of the soil. Originally in soil remediation experiments the polluted soil was placed in the desalination compartment as stationary and water saturated, e.g. (3). Later it has been shown that the best results with electrodialytic treatment fine-grained materials such as fly ash (12) and harbor sediment (13) were obtained when the material was treated in a stirred suspension instead of a stationary matrix. In the stirred system the removal of heavy metals was better and the overall resistance of the experimental cell was lower and more stable. Electrodialytic treatment of soil (the fine fraction) as stirred suspension has previously also shown very efficient for the removal of Pb (14). One advantage when using this setup is that the electrodialytic treatment can be combined with soil washing. In such case the clean coarser fraction and the highly polluted fine fraction is separated during the soil washing and the electrodialytic treatment is only used for remediation of the fine fraction. Another advantage is that it is fast and easy to change the soil environment by addition of chemicals to the suspension.

The principle of electrodialytic remediation of soil suspension is shown in Fig. 1. The soil is suspended in the central compartment and separated from the electrolytes in the electrode compartment by ion exchange membranes. Between anolyte and soil suspension is an anoin

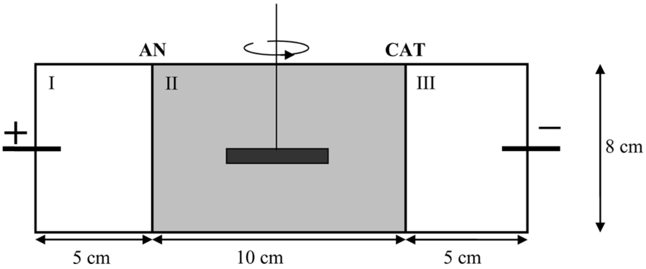


Figure 1. Principle of electrodialytic remediation of suspended soil. The contral (AN = anion exchange membrane, CAT = cation exchange membrane.

exchange membrane, which hinders passage of cations. Between the catholyte and soil suspension is a cation exchange membrane, which on the contrary hinders transport of anions. When the membranes are placed like this the main direction for electromigration is out from the suspension and into the electrode compartments.

MATERIALS AND METHODS

Experimental Soil

The soil was sampled from a Danish abandoned wood preservation site “Dansk A-Træ” situated in the northern Zealand, Denmark. At the site wood was preserved in the period 1960 to 1981 and since then the site has been unused. During the whole period the impregnation was performed with Boliden-K33 which is a CCA-oxide containing CuO, CrO_3 and As_2O_5. For the experiments about 15 kg soil was sampled from the dept of 2–15 cm close to the former storage area for the preservative. The soil was air dried in the laboratory before use in the electrodialytic experiments.

Analytical

Concentrations of Cu, Cr, and As in soil were measured after pre-treatment of the soil as described in Danish Standard 259 “Determination of metals in water, sludge and sediments – General guidelines for determination by atomic absorption spectrophotometry” where 1.0 g of dry soil and 20.0 mL (1:1) HNO_3 are heated at 200 kPa (120°C) for 30 minutes. The liquid was separated from the solid particles by vacuum through a 0,45 μm filter and diluted to 100 mL. The concentrations of Cu and Cr were measured with AAS. The As concentrations were measured with ICP.

Soil pH was measured in two ways by mixing 10.0 g dry soil and 25 mL 1.0 M KCl or 25 mL distilled water. After 1 hour of contact time pH was measured using a Radiometer pH electrode.

Organic matter The content of organic matter was found as a loss of ignition after 30 minutes at 550°C.

Water content of the soil was measured as weight loss after 24 hours in an oven at 105°C. Five duplicates of each of the analysis on the initial soil were made. On the treated soil three duplicates were made.

SEM-EDX analysis was performed on the untreated soil. For this analysis a small light green lump was crushed loosely by hand and placed directly on carbon tape before the analysis. No further pre-treatment of the sample was made prior to the analysis. The accelerating voltage of the SEM was 15 kV with large field detector (and X-ray cone). Different areas of the sample were investigated by SEM and the element distribution was examined by element mapping using EDX.

Concentration in Different Grain Sizes of Soil

The grain size distribution was made by sieving 100 g dry soil and on the concentrations of Cu, Cr and As were measured on the fraction in each sieve (pre-treatment and analyses as described above). The grain size fractions were: <63 μm; 63–75 μm; 75–125 μm; 0.125 –0.25 mm; 0.25–1.0 mm, 1.0–2.0 mm; 2.0–4.0 mm and >4.0 mm.

Release of Heavy Metals as a Function of pH

To examine the pH dependent extraction of Cu, Cr and As from the soil, the following procedure was used: 5.0 g dry soil (dried at 105°C for 24 hours) and 25 mL HNO_3 in various concentrations (from 0.01 M to 0.9 M) were suspended for 48 hours. The suspensions were filtered (0.45 μm) and the Cu, Cr concentrations were measured in the liquid phase with AAS, As with ICP. Extractions in distilled water were made as reference. Extraction in each concentration of acid was made in duplicate.

Electrodialytic Soil Remediation Experiments

The electrodialytic experiments were conducted in cylindrical cells as shown in Fig. 1. The cells were made from polymethyl methacrylate.

The cell had an internal diameter of 8 cm. The length of the central cell compartment was 10 cm and the length of the electrode compartments 5 cm. The ion exchange membranes separating the central compartment and electrode compartments were commercial membranes from Ionics (anion exchange membrane AR204 SZRA B02249C and cation exchange membrane CR67HUY N12116B). Platinum coated electrodes from Permascand were used. A power supply (Hewlett Packard E3612A) was used to maintain a constant current. In each of the electrode compartments 500 mL 0.01 M $NaNO_3$ adjusted to 2 with HNO_3 was circulated.

The soil was air dried in the laboratory and sieved through a 4 mm sieve before use in the remediation experiments. The water content of the soil was 3.2% ± 0.1% in all experiments before it was suspended. In every experiment 100 g air dried soil was suspended in 350 mL solution, corresponding to a liquid to solid ratio (L:S) of 3.6. The soil was kept suspended during the experiments by constant stirring with a plastic-flap attached to a glass-stick and connected to an overhead stirrer (RW11 basic from IKA). The suspension reached initially to about 3 cm below the hole where the stirrer was placed, but the height differed during each experiment.

During the experiments pH was adjusted in the electrode compartments to about 2 (once about every 24 hours). For the adjustment half-concentrated HNO_3 and 5 M NaOH were manually added to the catholyte and anolyte, respectively. Conductivity and pH in the soil suspension and the voltage between working electrodes were measured about once every 24 hours. For the pH and conductivity measurements samples were taken from the central compartment and the analysis were made with pH and conductivity electrodes where after the sample was returned to the central compartment.

By the end of the electrodialytic experiments the contents of Cu, Cr, and As in the different parts of the cell (membranes, soil, solutions, and cathode) were measured. The suspension from the central compartment was filtered. The sediment was dried and crushed lightly in a mortar by hand before the heavy metal concentrations (three samples) and pH (three samples) were measured. The contents of Cu, Cr, and As in membranes was measured after extraction in 1 M HNO_3 and rinsing of the electrodes prior to measurement was done in 5 M HNO_3. For some of the experiments the content of organic matter in the soil after treatment was measured.

The investigation includes 8 remediation experiments (Table 1) and covers removal of Cu, Cr, and As. Experiment A is a reference experiment where the soil was suspended in distilled water and no current was applied to the cell, but the setup and the procedure of maintaining

Table 1. Overview of electrodialytic experiments

Experiment	Soil suspended in solution of	Liquid: Solid	Current (mA)	Duration (days)
A	Distilled water	3.6	0	22
B	Distilled water	3.6	2.5	7
C	Distilled water	3.6	2.5	14
D	Distilled water	3.6	2.5	22
E	1 g I_2 in 350 ml	3.6	2.5	7
F	1 g I_2 in 350 ml	3.6	2.5	14
G	pH adjusted with HNO_3 to 1 soil suspension	3.6	5.0	7
H	pH adjusted with HNO_3 to 1 soil suspension	3.6	5.0	14

pH in the electrolyte solutions was the same as in the other 7 experiments. In experiments B to D the soil was suspended in distilled water and a constant current of 2.5 mA was applied. These three experiments differed in the duration only and the longest experiment (D) lasted 22 days as the reference experiment A. In experiments E and F the soil suspension was oxidized by addition I_2 to the suspension in the central compartment just before applying the electric field (1.0 g solid I_2 was added to the 350 mL distilled water) The solubility of I_2 in water is 0.3 g/L and to the central compartment I_2 crystals was added 2.8 g/L i.e., in excess. The soil suspension was acidified to pH 1 prior to the electrodialytic treatment in experiments G and H and the pH was maintained at 1 in the central compartment by addition of half-concentrated HNO_3 manually for approximately every 24 hours.

RESULTS AND DISCUSSION

Characterization of Soil and Pollution

Some characteristics of the experimental soil are given in Table 2 together with the Danish limiting values for Cu, Cr, and As for the most sensitive land use. It is seen that the soil was highly polluted with especially As in accordance to the limiting values and the limiting concentration for As was exceeded 170 times. The soil has a neutral pH and a relatively low carbonate and organic content revealing a low buffering capacity. The pH measured when the soil was suspended in KCl was lower than the pH measured in distilled water (0.7 pH units). This shows that H^+ ions were present in the exchangeable sites at the surface of the soil particles

Table 2. Characterization of experimental soil and Danish limiting values for most sensitive land use

	Cu (mg/kg)	Cr (mg/kg)	As (mg/kg)	Carbonate content (%)	Organic matter (%)	pH_{H_2O}	pH_{KCl}	Water content (%)
Soil	2170 ± 140	710 ± 70	3200 ± 350	1.60 ± 0.05	1.84 ± 0.61	7.3 ± 0.1	6.6 ± 0.1	3.21 ± 0.02
Limiting values	500	Cr(III) 500 Cr(VI) 20	20					

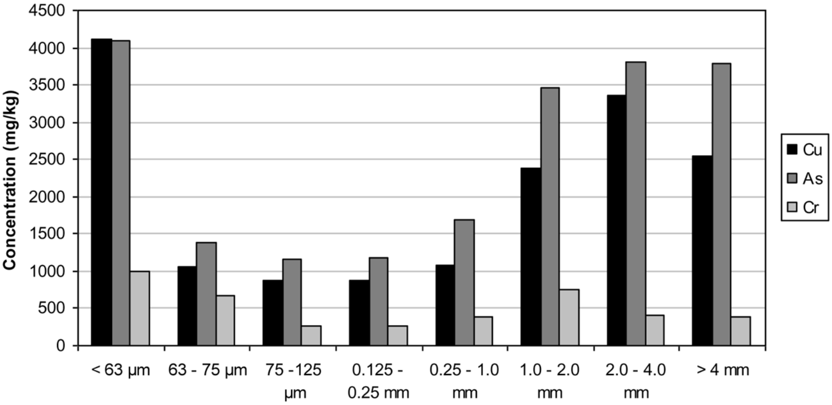


Figure 2. The concentration of Cu, Cr and As in the different size fractions of soil.

since more H^+ ions was released to the liquid in KCl (exchanged with K^+) than in distilled water.

The highest concentration of the three pollutants was found in the fine fraction (<63 µm) (Fig. 2). This fraction accounts for about 35% of the soil per weight. The next fractions until 1.0 mm were the least polluted and these fractions accounted for about 50% in weight. The three fractions larger than 1.0 mm were again highly polluted (10% weight of the soil). In general heavy metals are expected to concentrate in the fine fraction of soils due to the larger surface area here and the higher number of adsorption sites, but that was not the case in the actual soil. The sieving procedure for this investigation was made on dry soil and thus the grain size separation is not complete since the larger particles to some degree are covered by dust of smallest particles. This means that the concentrations measured in the larger fractions are probably little higher than the true concentrations since the concentrations in the dust particles are higher than the concentration of the particles of the actual fraction. This, however, cannot explain the high concentration in the fractions larger than 1.0 mm. Visually some light green particles from about 1 mm in diameter were seen in the soil. The particles were loosely bound together and easy to break. SEM-EDX mapping analysis was made to see the elements in these green particles and an example is shown in Fig. 3. EDX elemental mapping of the area showed that the particle contained Cu, Cr, and As and together with the corner of another particle (lower left in the SEM picture) the particle consisted of 8.2% Cu, 0.4% Cr, and 10.0% As together with 58.4% O, 4.3% Al,14.1% Si, 2.8% K, 1.7% Fe. The result from the elemental mapping is also shown in Fig. 3. The particle itself contained Cu, Cr, and As whereas the part of the other particle

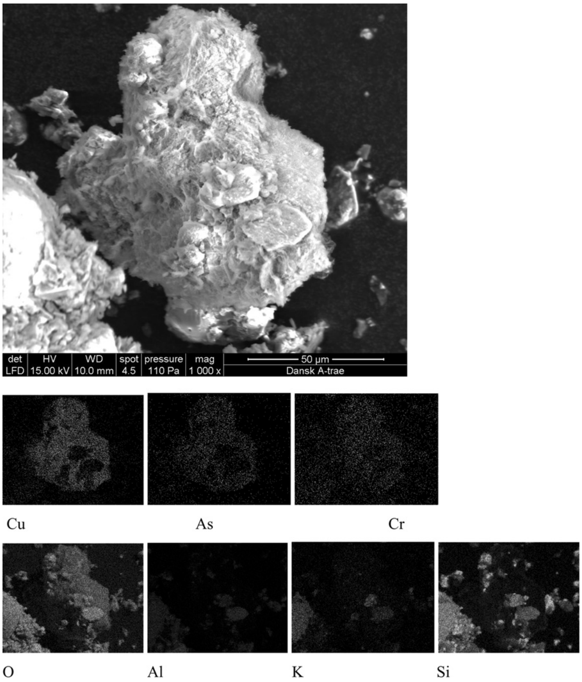


Figure 3. SEM picture of green soil particle and result from EDX mapping.

(lower left corner) do not contain these three. Oxygen is a part of both particles. The particle itself is thus formed from the same elements Cu, Cr, As, and O as the original Boliden-CCA, which was used in the impregnation process at the site. From the SEM picture it is seen that three small particles (of size in the silt fraction) are build into the surface of the particle. Where these particles are situated no Cu, Cr, or As was detected, but Al, Si, and K was together with O. These particles are ordinary soil particles and composed of the same elements as the particle in the lower left corner. It seems from the SEM/EDX analysis as well as from the visual inspection of the light green particles as if the soil particles are cemented together by a CCA-oxide solid phase. More particles were investigated as the one in Figure 3, and most showed similar composition, except from not all of them containing a measurable amount of Cr.

Desorption as a Function of Acidification

Figure 4 shows the concentrations of Cu, Cr, and As extracted from the soil at different pH values. The mean initial concentrations are indicated,

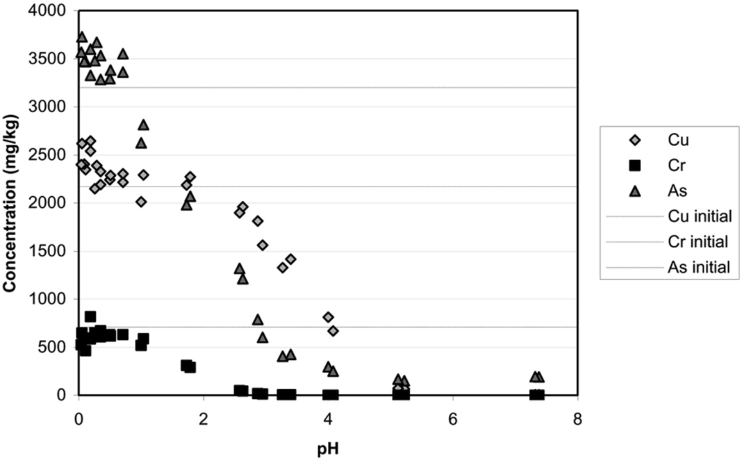


Figure 4. pH dependent desorption of Cu, Cr and As from soil in extractions of HNO_3.

too. At neutral pH of the suspension (in distilled water) no measurable amount of Cu and Cr was extracted, whereas about 100 mg As/kg was extracted. This does not necessarily indicate that such concentration was mobile in the soil before the sampling. Mobile As is expected washed out to deeper soil layers in the 25 years (at lest) since the spill. The aeration of the soil sample during sampling and treatment may likely have influenced the mobility of As. The SEM-EDX investigation showed that As and O were both present in the green precipitates of pollution and there may be some arsenious anhydride (As_2O_3) present, which is soluble, thermodynamically stable in the presence of water and acid, neutral and slightly alkaline solutions, but only in environments free of oxygen (15). In contact with the atmosphere and in neutral and acidic environments As_2O_3 is oxidized to H_3AsO_4 or $H_2AsO_4^-$ dependent on pH (the first in the most acidic environment). The fact that As was extractable from the soil in distilled water indicates that there is a potential risk for mobilization of As if the soil is excavated.

As the pH decreases, the extraction of Cu, Cr, and As increases. At pH values below about 4.5, Cu extraction starts and it reaches about 100% at approximately pH 2. The As extraction is increasing fast as pH is decreased from pH about 3 and reaches about 100% at pH of about 1. Cr extraction starts even lower, at pH about 2, but approximately 100% extraction is also reached at pH 1. Thus at pH below 1 all three elements are extracted to a level comparable to what can be extracted by acid digestion.

Electrodialytic Experiments Overall Results

An overview of the results from the electrodialytic remediation experiments is given in Table 3. The measured concentrations of Cu, Cr, and As in the soil at the end of the experiments are given with standard deviations. The recovery of an element is defined as the relation between the sum of mass found in the different parts of the cell at the end of the experiment and the initial mass calculated on basis of the mean initial concentration (given in Table 2). The removal in percentage for each element is calculated as mass of the actual heavy metal in the soil and solution in the central compartment divided by the total mass found in all parts of the cell at the end of the experiment.

The soil was automatically acidified during every experiment. The final pH of the soil measured after suspension in distilled water and KCl are given in Table 3. The pH measured in KCl was 0.6 to 1.0 pH units lower than pH measured in distilled water and this is in general a little larger difference than initially. The difference shows that H^+ ions are present in the exchangeable sites to a higher extent even than before eletrodialytic treatment.

The pH and conductivity of the soil suspension measured during the experiments are shown in Figs. 5(a) and 5(b), respectively. It is noticed that there is a difference in the initial pH of experiments A to F where it could be expected to be very similar. The procedure when starting the experiments was the same. The duration from suspending the soil in the central compartment to applying the current varied slightly, but it was never more than about 30 minutes. The pH decreases fast in the suspension even without current (experiment A) and the difference in initial pH can be due to the small difference in time before application of current due to diffusion of H^+ ions from the acidic catholyte over the cation exchange membrane. The fast decrease of the pH in the soil suspension shows that this soil does not have a high buffering capacity as in the case of soil fines from a Pb polluted soil rich in carbonates (about 17%) where the decrease in pH occurred after 12 days (14) even though the current density was 8 times higher than in the experiments of the present paper.

The pH of the soil suspension in experiments B and C did not reach the same low level as in the other experiments where pH was not adjusted directly in the soil suspension (A and D to F). The final soil pH of experiments B and C was also higher (Table 3). The acidification of the soil suspension in the central compartment is mainly due to diffusion of H^+ ions over the cation exchange membrane from the catholyte, however, the diffusion is not free to occur since anion are not allowed to pass this membrane. That means that in order to maintain electroneutrality the

Table 3. Cu, Cr, and As concentrations in soil after treatment. Recovery is the relation between heavy metals in the different parts of the cell at the end of the experiments divided with the initial amount in the soil. Removal is the amount of the heavy metal in the soil and solution in the middle compartment divided with the total amount of the heavy metal found at the end of the experiment

Experiment	Cu (mg/kg)	Cr (mg/kg)	As (mg/kg)	Recovery (%) Cu/Cr/As	Removal (%) Cu/Cr/As	Organic matter (%)	pH H_2O/KCl
A	230 ± 24	770 ± 65	2400 ± 570	95/121/98	67/9/19	1.5	4.2/3.2
B	530 ± 21	650 ± 12	1540 ± 5	100/91/109	77/4/59	1.4	4.4/3.6
C	320 ± 6	510 ± 49	1040 ± 40	91/87/87	86/14/67	n.m.	4.5/3.7
D	110 ± 6	530 ± 25	1400 ± 90	100/95/91	95/28/57	1.5	4.0/2.8
E	320 ± 50	570 ± 110	1750 ± 270	91/85/91	81/8/30	1.6	3.7/3.1
F	220 ± 30	720 ± 70	1530 ± 250	92/118/100	90/11/49	1.3	3.9/2.9
G	170 ± 17	220 ± 20	2870 ± 400	88/90/106	64/46/7	n.m.	3.8/3.1
H	80 ± 14	160 ± 17	1070 ± 170	82/83/87	81/51/50	n.m.	3.8/3.0

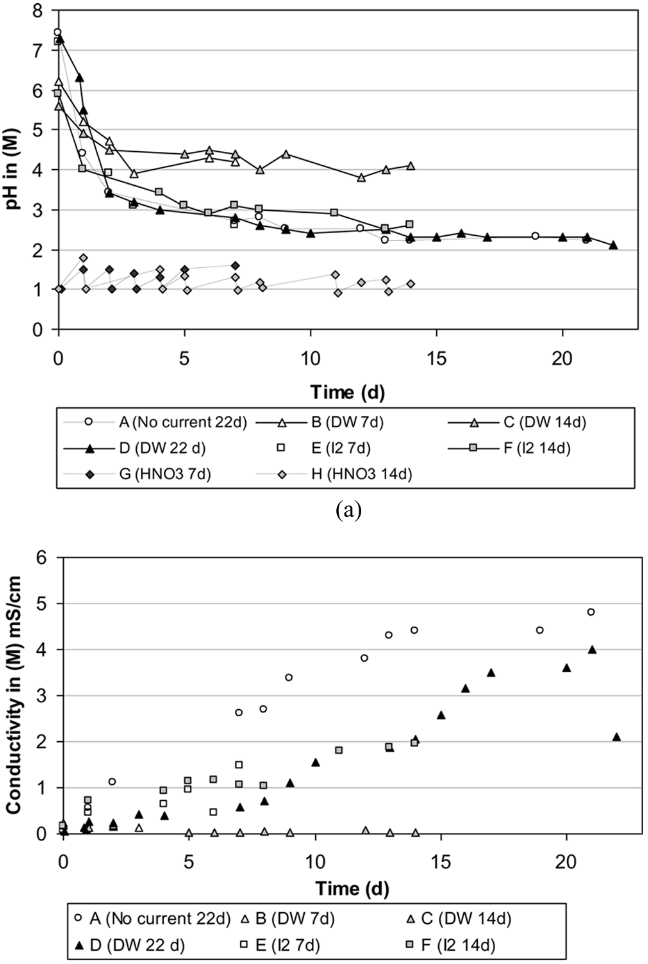


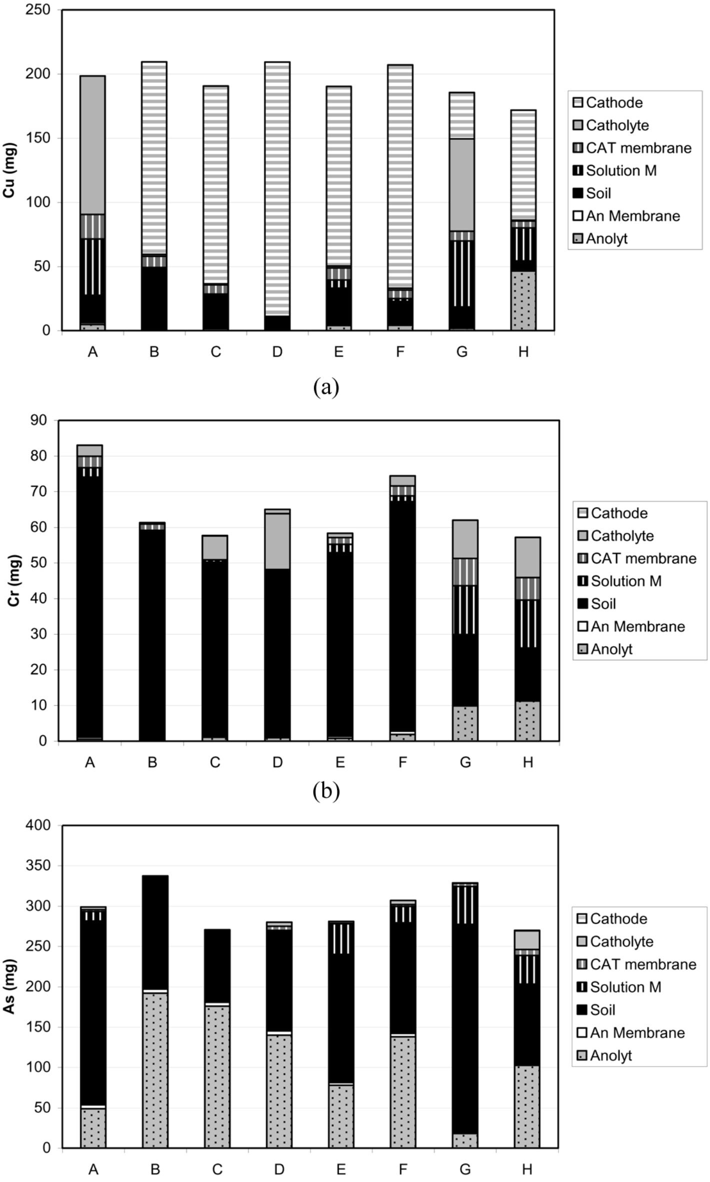
Figure 5. (a) pH and (b) conductivity in the soil suspension during the electrodialytic treatment.

H^+ ions from the catholyte can only exchange with positive ions from the suspension. In all experiments the catholyte was acidic and available H^+ ions was never a limiting factor. The conductivity of the soil suspension was low all through the remediation in experiments B and C compared to the other experiments (Fig. 5b) and these are also the experiments with the highest pH all through. The higher pH is a reason for the lower conductivity due to a smaller H^+ ion concentration but it may also be a key to the limited acidification because of a limited amount of cations for exchange with H^+ ions from the catholyte. Exactly why experiments B and D differs from experiment C in the acidification pattern of the soil suspension is not known since the experimental conditions of these experiments were very similar. In experiment A, however, there was no current for simultaneous removal of the H^+ ions from the soil suspension. This means that acidification of the soil suspension occurred, aiding desorption and dissolution processes for release of new ions from the soil and subsequent exchange over the cation exchange membrane for further acidification. In experiments E and F, I_2 was added to the soil suspension and the oxidation reactions probably released ions from the soil for exchange with H^+ ions from the catholyte.

Figures 6(a) to 6(c) shows the distribution of Cu, Cr, and As in the cell at the end of the experiments. Overall the distribution pattern of the three elements differs significantly. In most experiments the major part of the Cu was found at the cathode, the major part of Cr remained in the soil whereas for As the major part was about equally distributed in soil and anolyte. These different patterns underline the different chemical behavior of the three elements.

The recovery was between 82% and 118% and the variation is due to the inhomogeneous distribution of the pollutants in the industrially polluted soil. The variation of mass of the three elements at the end of the experiments is seen from Figs. 6(a) to 6(c). The standard deviations for the initial concentrations are given in Table 1 and calculated on basis of the mean initial concentrations and these standard deviations, the mass of the pollutants in the cell should between: 197–224 mg Cu (mean 210 mg Cu); 61–77 mg Cr (mean 68 mg Cr) and 276–344 (mean 310 mg As). The mass of Cu at the end of all experiments falls within these limits (Fig. 6(a)). For Cr the mass exceeds the upper limit in experiment A where 83 g Cr was found, whereas for experiments D and H the Cr mass was below the lower limit (58 g and 57 g respectively). For As the mass at the end of the experiments (Fig. 6(c)) was within the limit except for experiments C and H where 270 mg As was found in both. The mass balances for the experiments are considered in an acceptable range since the mass of the elements in most experiments are within the range given from the standard deviation of the initial concentrations and the few cases which are outside are very close to the limits.

To evaluate if there is an advantage in electroremediation in the stirred system compared to electroremediation of a stationary soil, the assessment of the volume treated per time unit and per energy unit is necessary. This means that if the volume of the soil suspension is e.g. four times the volume of water saturated soil, the remediation should be at



(a)

(b)

(c)

Figure 6. Distribution of (a) Cu, (b) Cr and (c) As in the different parts of the electrodialytic cell at the end of the experiments.

least 4 times faster in the stirred system to avoid increase in the size of the treatment plant. Experiments for direct comparison of duration and volume in the two systems have not yet been conducted, but the duration of the experiments in the stirred cell of the present investigation can roughly be compared with (3) in what regards Cu remediation. The experiments in (3) were conducted in a stationary electrodialytic cell with a wood preservation soil with low carbonate content as the present. In (3) about 1.5 cm soil was remediated for Cu (<500 mg/kg) in 12 days at 10 mA. In the present experiments with soil suspended in distilled water, the soil was remediated for Cu in between 7 and 14 days so the duration seems similar for a similar volume (100 g dry soil corresponds to 1.25 cm soil in a compartment of 8 cm in diameter). However, the current density was 4 times less in the stirred experiments and the voltage was generally less as well. Thus the energy consumption was less per unit weight of treated soil when using the stirred setup. A thorough comparison is though needed.

Removal of Copper

Except from experiment B (1 week electrodialytic treatment and soil suspended in distilled water) the Cu concentration in the soil at the end of treatment was less than the limiting value of 500 mg/kg and Cu. The removal percentages for Cu were between 64% and 95%. Of the three pollutants, Cu was the easiest to remove. The copper removal started after 1–2 days in every experiment since it was noticed that the surface of the cathode changed to red which is a sign of electro-precipitation of Cu. The most efficient Cu removal was obtained in experiment D where the soil was suspended in distilled water and the current was applied for 3 weeks. In this experiment the final soil concentration reached was 110 mg Cu/kg and the removed Cu was almost exclusively found at the cathode i.e., the separation was very efficient. An even lower Cu concentration of 80 mg/kg was reached in experiment H (where pH was adjusted to about 1.0 in the soil suspension and current was applied for 2 weeks), but in this experiment the current strength was the double as in experiment D and thus the charge transfer was higher. Further Cu was found in all parts of the cell at the end of experiment H and especially the Cu in the solution of the central compartment means a poorer separation process since all solutions are polluted with Cu. It is seen that Cu was transported towards the anode to a high extent in experiment H as the only experiment. The ion exchange membranes are efficient down to a pH of about 1 (as pH was in the central compartment in this experiment) and diffusion of Cu over the anion exchange membrane can occur if the membrane is not working well and this may be what has happened in experiment H.

The addition of I_2 to the soil suspension did not influence the Cu removal (comparison of experiments B and E as well as C and F). The addition of acid on the other hand decreased the Cu removal efficiency probably mainly because the increased amount of H^+ ions decreased the transference number of Cu^{2+}. A longer duration than the 2 weeks in experiment H might have emptied the solution of the central compartment for Cu. Another possibility for improving the remediation conditions could be to limit the addition of acid to a pretreatment and not add acid to the suspension during the treatment.

This would decrease the influence of the H^+ ions on the transference number of Cu. Even in the dialytic experiment A (without current) a low concentration of Cu was reached (230 mg Cu/kg). In this experiment, however, the separation process was poor and a high concentration of Cu remained in the solution of the central compartment. There is no force driving this Cu out when equilibrium has been reached and the separation will not improve unless an electric field was applied afterword.

Removal of Chromium

In the majority of soils, the relatively insoluble and less mobile Cr(III) form predominates over Cr(VI) mainly because Cr(VI) is a strongly oxidizing species and in the presence of soil organic matter Cr(VI) is reduced to Cr(III) (16). In the SEM-EDX investigation of the present soil Cr and O was always identified together (an example was given in Fig. 3) and this together with the low extractability of Cr at pH higher than about 1 (Fig. 4) may indicate that Cr(III) occurs in the present soil as insoluble hydroxides and oxides, as can generally be expected according to (16). In experiments B to D where the soil was suspended in distilled water the removed part of Cr was mainly transported towards the cathode revealing Cr(III) since this form is positively charged. Cr(VI) is the more stable form of chromium in equilibrium with atmospheric oxygen (16), but in these experiments there was no evidence for oxidation of the desorbed Cr(III) to Cr(VI) since the Cr was transported mainly towards the cathode.

The initial concentration of Cr (710 mg/kg) was close to the limiting value for Cr(III) (500 mg/kg), but even though the percentage of Cr necessary to remove in order to meet the limiting value was only 31%, the limiting value was only met in few of the experiments. The removal percentages for Cr were between 4% and 51%. After 3 weeks of electrodialytic treatment of soil suspended in distilled water the limiting value was almost reached. However, an advantage of electrodialytic remediation of suspended soil compared to remediation of stationary soil is the possibility of faster remediation, and 3 weeks is considered too long.

Cox et al. 1996 (17) and showed successful mobilization of elemental Hg by oxidation with I_2 prior to electroremediation. In these experiments I^- and I_2 was added in the catholyte and the Hg oxidation was dependent on electromigrating I_3^- ions. In the present investigation it was tested if it was possible to oxidize adsorbed Cr(III) to the more mobile Cr(VI) by addition of I_2 crystals and obtain faster and better Cr removal under strong oxidizing environments (Cr(V) is present in ionic form in a wide range of pH). In the stirred cell the I_2 crystals could be added directly into the soil suspension which improves the effect since oxidation is not dependent on electromigration as in the eperiments by Cox 1996. The added amount of I_2 (2.86 g/L) exceeded the solubility of the solid I_2 crystals (0.3 g/L at 20°C) and was expected that there was a pool of I_2 crystals for oxidation reactions during the experiments. No positive effect of the I_2 addition was seen on the Cr removal (Table 3) compared to the first experiments with distilled water in the central compartment and only slightly more Cr was transported towards the anode and the oxidation was insufficient. The I_2 might have been wasted for oxidation of organic matter in the soil, but the organic matter content in the experiments with I_2 addition was not varying significantly from the other experiments (Table 3). The tubes circulating the anolyte became yellow after few hours of experiment and the intensity of coloring increased during the experiments to a dark red color. Coloring was not seen in other experiments than those with I_2 addition to the soil suspension and this reveals a chemical reaction between iodide and the tubes or a reaction for which the presence of I_2 has been a catalyst. The idea of oxidizing Cr(III) in the present soil with I_2 was turned down. Higher concentration of I_2 might give a better result, but the use of I_2 would then be unrealistic in full scale (in the experiments conducted here the I_2 addition already corresponded to10 kg I_2 per ton soil to be treated, which is a high concentration and which may be considered as a new pollution).

Instead it was investigated if initial acidification of the soil suspension to $pH = 1$ could mobilize Cr to the necessary extent (experiments G to I), since it was seen from the pH-desorption test that most Cr was desorbed from the soil at pH below 1 (Fig. 4). This initial acidification resulted in sufficient reduction in Cr concentration during the electrodialytic treatment. In experiment H the concentration reached was 160 mg Cr/kg which is well below the limiting value. The separation, however, was not sufficient and about 1/4 of the Cr was found in the solution in the central compartment at the end of the experiment. The experimental conditions must be optimized as described for Cu to remove the Cr from the solution in the central compartment. It is seen, that Cr was removed towards both anode and cathode in experiments G and H where pH was maintained 1 in the central compartment. The HNO_3 is an oxidizing acid and this may be the reason for Cr to move towards the anode as Cr(VI). (18) found simultaneous removal of Cr towards anode and cathode when electro-remediating an industrially polluted soil. Whether the transport in the present experiments is mainly due to electromigration or a combination of electromigration/diffusion due to damaged anion exchange membrane as suggested above cannot be extracted from these experiments.

Removal of Arsenic

The Danish limiting concentration for As in soils at most sensitive land use is 40 mg/kg (Table 2) and from Table 3 it is seen that the As concentration after the electrodialytic experiments still far exceeds this limit. The lowest concentration obtained was 1040 mg As/kg (corresponding to a removal of about 68% As). It is seen from Fig. 6(c) that the major part of the removed As was removed towards the anode in every experiment as expected. In the electrodialytic experiments where the soil was suspended in distilled water (experiments B to D) there was no As left in the solution of the central compartment meaning that the limiting step for the removal was desorption of As. In these experiments the pH of the suspension reached about 4 (experiments B and C) and 2.2 (experiment D) and at these pH values about 20% and 50% As, respectively, could be expected desorbed according to Fig. 4. From the dialytic experiment (experiment A) where no current was applied it seems however to be less. In this experiment the pH of the soil suspension also reached about 2.2 but still about 3/4 of the As remained adsorbed to the soil. The electrical field increased the desorption and removal of As compared to the dialytic experiment and the reason is probably that an equilibrium situation was not reached in the soil suspension since the desorbed As was removed simultaneously to the desorption, forcing more As to be desorbed. However, there was a limit for desorption and there was no improvement between remediation for 1 week and 3 weeks.

When adding I_2 and hereby increasing the oxidation state of the soil suspension (experiments E and F) the mobility of As for electromigration decreases compared to suspension in distilled water, seen from the fact that in these two experiments As remains in the solution of the soil suspension and is no longer transported towards the anode when first desorbed. This may indicate that uncharged As species are present and this could very likely be H_3AsO_4 (which is prevailing at high oxidation states and low pH less than about 2 (7)) or the transference number of As is decreased due to the I_2 addition and following increased conductivity. Acidifying the soil suspension prior to application of current also meant decreased electromigration of As and the reasons could be the same as in the experiments with I_2 addition, since there also was an acidic and oxidizing environment in the soil suspension here (HNO_3 is an oxidizing acid). At pH of 1 the major part of As was expected desorbed in accordance to Figure 4, but it seemed not to be the case in the electrodialytic experiments, especially the desorption in experiment G was limited compared to the expected.

Simultaneous Removal of Cu, Cr, and As

Simultaneous removal of Cu, Cr, and As was obtained during the electrodialytic treatment of soil suspension. The best results were obtained in experiment D (soil suspended in distilled water and remediation for 3 weeks and remediation at 2.5 mA) and H (soil suspension adjusted to pH 1 with HNO_3 and remediation for 2 weeks at 5 mA). Based on the soil concentrations 95% Cu, 28% Cr, and 56% As was removed in experiment D and 96% Cu, 74% Cr and 61% As in experiment H. The removal percentages was thus highest in experiment H but the separation was not as good as in experiment D, where neither of the elements were found in the solution of the soil suspension. In experiment H acid was added to the central compartment several times during the experiment to maintain pH at about 1 and this acid addition may not be necessary but instead it may hinder sufficient removal of the desorbed pollutants from the central compartment due to decreased transference numbers of the pollutants. Better separation could probably be reached if the soil suspension was only acidified to about 1 prior to the electrodialytic treatment.

In neither of these experiments, however, the limiting value for As in the soil was reached. The final concentration in experiment H was 1070 mg As/kg, which is much higher than the limiting value of 40 mg As/kg. There is nothing in the electrodialytic experiments of the present investigation that indicates that minor changes of the remediation parameters would enable reaching this low limiting value. As efficient electrokinetic removal of As from soil have been obtained in alkaline environments, it should be tested if maintaining a high pH in the suspension after or before the acidic environment for removal of Cu and Cr could give a sufficiently low As concentration. In this case the idea of simultaneous removal is not fulfilled, but pH changes in the stirred suspension is easily obtained compared to in stationary cells, and an overall fast remediation might be obtained even though the remediation occurs stepwise at two different pH values.

CONCLUSIONS

Electrodialytic removal of Cu, Cr, and As from soil polluted from wood preservation industry was conducted in laboratory cells where the soil was remediated as a stirred suspension. Simultaneous removal of the pollutants was shown possible and the best removal percentages reached were 95% Cu, 74% Cr, and 61% As. The final concentration of As in the soil after treatment did not meet the Danish limiting value, and further development of the method is needed to improve the As removal. The final concentrations of Cu and Cr, on the other hand did meet the limiting values.

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